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Shock induced formation of $MgAl_2O_4$ spinel from oxides

David K Potter* and Thomas J. Ahrens

Seismological Laboratory 252-21, California Institute of Technology, Pasadena, California

Abstract. The physics of mineral grain sliding, which occurs upon dynamic compression of rocks, is investigated by shock loading single crystals of corundum (Al_2O_3) and periclase (MgO) in contact obliquely in impact experiments. Energy dispersive X-ray analysis and X-ray diffraction studies of samples recovered from 26 - 36 GPa, 800 ns experiments indicated that under certain conditions a spinel phase of composition $MgAl_2O_4$ and thickness ≤ 20 μm was produced at the interface between the two crystals. Although the computed shock (continuum) temperatures were below those necessary to melt the initial oxides, the spinel nonetheless appears to have formed as a result of localised melting, via grain boundary sliding friction, followed by rapid quenching. Scanning electron microscopy (SEM) revealed some evidence for such melting. Moreover, the timescale of the experiments is too short for solid state diffusion (during the shock state) to explain the observed spinel thickness, although defect enhanced solid state diffusion, subsequent to loading and unloading, remains a possibility. The results also reinforce other recent observations and theories of heterogeneous deformation in minerals.

Introduction

Observations of the response of mono- and polymineralic rocks and meteorites to shock loading have long suggested that, at shock pressures substantially below those required to induce complete melting, the irreversible work carried out on such media was deposited very inhomogeneously. Theories of shock deformation of brittle minerals such as SiO_2, MgO and Al_2O_3 [Grady, 1980; Grady and Kipp, 1987] have suggested that, rather than shock deformation occurring uniformly (as implicit in continuum thermodynamics) heterogeneous deformation along shear bands takes place. Evidence for such heterogeneous deformation has been inferred from framing camera photographs and measured in situ temperatures, which were greater than the calculated continuum temperatures, in shock experiments on NaCl, KCl, LiF, $CaSO_4$. $2H_2O$, $CaCO_3$, MgO, SiO_2 and Al_2O_3 [Brannon et al,. 1983; Kondo and Ahrens, 1983; Schmitt and Ahrens, 1983; Schmitt et al., 1986]. The observed high temperatures, often sufficient to produce melting, were assumed to be generated through grain sliding friction along shear bands. Melting along grain boundaries, as observed in scanning electron micrographs (SEM), was possibly responsible for the results of Kondo et al [1986] who shock produced cubic aluminium oxynitride spinel (5 AlN . 9 Al_2O_3) from initial fine powder AlN/Al_2O_3 mixtures.

However, not all shock loading experiments have been interpreted in this way. Experiments on porous mixtures of ZnO and Fe_2O_3 which produced Zn_{1-x} Fe_x Fe_2O_4 spinel [Venturini et al., 1985; Morosin et al., 1986] were interpreted in terms of a solid state reaction. This interpretation arose largely because the calculated continuum temperatures were lower than the melting points of the initial oxides.

The present work in which we examine the formation of spinel ($MgAl_2O_4$) from corundum (Al_2O_3) and periclase (MgO) was in part motivated by the above observations as well as the fact that shock induced spinel (ringwoodite) and garnet occurs in veins of melted material in the shocked meteorite Tenham [Binns, 1970]. In this case the $(Mg, Fe)_2SiO_4$ spinel is the product of the effect of both high pressure and temperature. However in the present experiments the formation of spinel appears to be strictly the result of high temperature and not high (shock) pressure. Spinel found in spherules from Cretaceous/Tertiary boundary sediments also appears to have formed as a result of high temperature followed by rapid crystallization from molten silicate droplets produced from a major impact event [Kyte and Smit, 1986]. The spinel is distinguished from typical terrestrial spinel by exhibiting high Mg, Al, Ni and Fe_2O_3/FeO and relatively low Ti and Cr, with solid-solution compositions ranging from nearly pure magnetite to magnesioferrite to relatively pure $MgAl_2O_4$ spinel. Similar spinels have been found from a late Pliocene asteroid impact in the Southern Ocean [Margolis et al., 1991]. Recently, reflectance spectra data have indicated the presence of $MgAl_2O_4$ spinel in the surface regoliths of two asteroids [Burbine et al, 1992], and various origins for this spinel were put forward. Perhaps an as yet unconsidered possibility is the shock production of spinel due to impact events on the surface of the asteroids. Our present study demonstrates that $MgAl_2O_4$ spinel can be produced by grain boundary sliding of single crystal Al_2O_3 on single crystal MgO induced by oblique impact. Although we will show that the calculated shock continuum temperatures are below the melting points of the initial constituents, we will suggest that grain sliding frictional melting has occurred. The temperature generated via friction at the interface between two sliding crystals can be substantial, even for relatively slow sliding speeds [Jaeger, 1942; Bowden and Tabor, 1968]. Investigating individual grain boundary sliding in this way might also improve our understanding of the physics of dynamic powder compaction of hard substances such as diamond [Potter and Ahrens, 1987] and ceramic powders, although our experimental configuration is only an approximate analogue of an interface between two powder particles.

Experimental Details

Single crystals of Al_2O_3 and MgO, each 1.25 cm in diameter and 0.05 cm thick, were placed in contact at an angle θ in a stainless steel capsule (Figure 1). A stainless steel flyer plate (1.59 cm in diameter and 0.25 cm thick) was accelerated to a velocity of between 1.50 and 1.81 km/s using the Caltech 20 mm gun and impacted against the capsule. This induced sliding of the crystals along their plane of contact. The experimental conditions for each shot are summarised in Table 1. Initial shock states in the two crystals are shown. Shock pressures (P_H) were obtained by the impedance matching technique [Zeldovich and Raizer, 1967] using the following shock (U_s) and particle (u_p) velocity data of Pavlovskii [1971] for Al_2O_3 of density 3.92 Mg/m^3 (actual measured density was 3.89 Mg/m^3),

$$U_S \text{ (km/s)} = 8.60 + 0.76\, u_p \quad (1)$$

*Now at: Department of Physics, The University, Newcastle upon Tyne, England, NE1 7RU.

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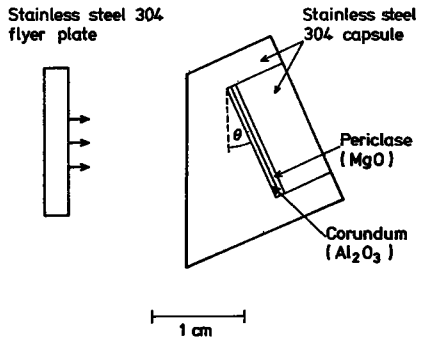

Fig. 1. Cross-section of experimental target assembly.

and the data of Marsh (1980) for MgO of density 3.58 Mg/m^3,

$$U_S \text{ (km/s)} = 6.60 + 1.37\, u_p \quad (2)$$

The initial shock states shown for MgO took account of the fact that the shock wave passed initially through Al_2O_3. Shock (continuum) temperatures T_H were given by [Zeldovich and Raizer, 1967],

$$T_H = T_S + \frac{V_H (P_H - P_S)}{\gamma C_V} \quad (3)$$

where T_S and P_S are the temperature and pressure along the prinicipal isentropes, V_H is the high-pressure specific volume, γ is the Grüneisen parameter and taken to be 1.6 for MgO [Anderson et al., 1968] and 1.5 for Al_2O_3, and C_V is the specific heat at constant volume (assumed to be the Dulong-Petit value $C_V = 3R$ where R is the gas constant). Table 1 shows that the theoretical continuum temperatures were lower than those necessary for melting. Weast [1982] gives melting temperatures of 2072 K and 2852 K for Al_2O_3 and MgO respectively. (Some variation in quoted values exists with Grady, 1980, giving values up to 250 - 300 K higher). Although the shock wave interactions with the sample layers are relatively complex (involving complex shock refractions etc.) the T_H values given in Table 1 represent the maximum estimates of the continuum temperatures produced in the samples. These are consistent with previous data on similar materials [Grady, 1980; Schmitt and Ahrens, 1983]. However, localised higher temperatures (sufficient for melting) almost certainly occurred at the crystal - crystal interface as will be discussed below.

Microanalysis of Recovered Samples

Scanning electron microscopy (SEM), optical microscopy and energy dispersive X-ray analysis was initially performed on polished sections of the recovered samples. Extensive analyses did not indicate the formation of spinel from shots 884 and 919, however the energy dispersive X-ray analysis strongly suggested the presence of spinel at the interface between the Al_2O_3 and MgO single crystals in shot 905.

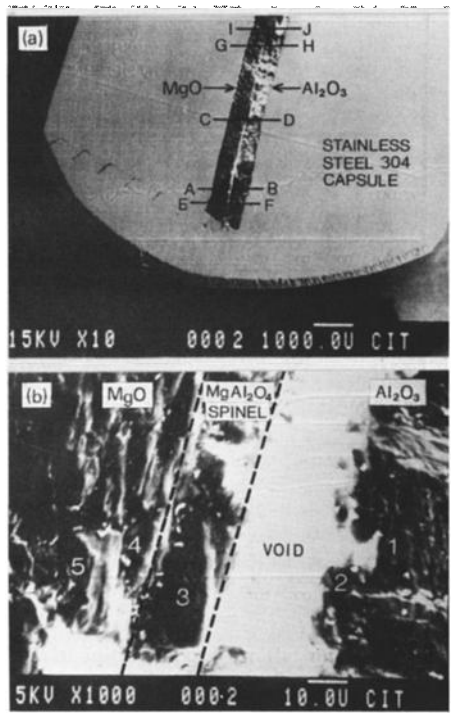

Fig. 2. SEM images of the recovered sample from shot # 905. (a) Indicates sections analysed by energy dispersive X-ray analysis (results in Table 2). Scale bar = 1000 μm. Flyer plate impacted on right hand side of capsule. (b) Magnified view of section AB. Scale bar = 10 μm.

Several points along the interface yielded an elemental ratio of aluminium to magnesium very close to 2:1, consistent with $MgAl_2O_4$ spinel. Typical analyses of areas shown in Figures 2(a) - (b) are given in Table 2. The values given are averages of a number of readings (as shown) along with the standard deviation, each reading being taken in a slightly different area. Readings at the interface were taken along a line perpendicular to the plane of contact of the initial crystals, so that the area analysed was significantly greater than the 2 μm diameter beam spot size. This enabled estimates of the thickness of the spinel layer to be determined, and also ensured that the results were not merely an artifact of being at the interface but were more likely to be genuine spinel compositions. Slight deviations of the elemental ratio Al/(Al + Mg) from the theoretical value of 2/3 for spinel were most likely caused by the X-ray beam not being exactly perpendicular to the sample surface (which was difficult to make perfectly smooth). Spinel was not detected everywhere along the interface, but was more apparent where there was some evidence for localised melting (e.g. near interfaces of sections CD and IJ - see Figure 4(a)).

Table 1. Experimental conditions and calculated shock pressures and temperatures.

Shot number	Oblique angle θ (degrees)	Projectile velocity (km/s)	Shock pressure P_H[a] (GPa)		Shock continuum temperature T_H (K)		Recovered Sample Condition
			Al_2O_3	MgO	Al_2O_3	MgO	
884	15	1.50	30	26	390	410	No spinel detected.
905	15	1.81	36	32	990	510	Spinel ≤ 20 μm thick at Al_2O_3/MgO interface. SEM evidence for melting.
919	25	1.81	36	32	990	510	No spinel detected. Some 'missing mass' possibly due to localised vaporisation.

[a]Initial shock states.

Table 2. Energy dispersive X-ray analysis of areas indicated in Figure 2 (shot # 905). Values of the elemental ratio represent averages of a number of readings (as shown) along with the standard deviation.

Area of analysis (section, position)	Elemental ratio Al/(Al + Mg)	Interpretation from analysis and SEM observations
AB 1	0.99 ± 0.01 (2)*	Al_2O_3
AB 2	0.98 ± 0.01 (2)	Al_2O_3
AB 3 Interface	0.63 ± 0.03 (5)	$MgAl_2O_4$ spinel ≤ 20μm thick.
AB 4	0.07 ± 0.01 (3)	MgO
AB 5	0.08 ± 0.01 (3)	MgO
CD Interface	0.66 ± 0.01 (3)	$MgAl_2O_4$ spinel ≤ 10 μm thick. SEM evidence for melting.
EF Interface	0.62 ± 0.03 (4)	$MgAl_2O_4$ spinel ≤ 10 μm thick.
GH Interface	0.45 ± 0.05 (3)	No spinel. No evidence of melting. Analysis merely represents fractions of original crystals.
IJ 1	0.98 ± 0.01 (3)	Al_2O_3
IJ 2 Interface	0.71 ± 0.03 (4)	MgAl2O4 spinel ≤ 10 μm thick. Some evidence for melting.
IJ 3	0.12 ± 0.03 (4)	Mainly MgO
IJ 4	0.01 ± 0.01 (3)	MgO

*Numbers in brackets indicate number of separate analyses.

Confirmation of spinel in the recovered sample from shot 905 was provided from Debye-Scherrer X-ray diffraction analysis using a Siemens D-500 diffractometer. Material recovered near the interface was carefully removed and placed on glass slides for analysis. One such analysis, revealing several spinel diffraction lines, is shown in Figure 3. Other microsamples gave stronger but fewer spinel diffraction lines, whilst some samples only showed peaks associated with Al_2O_3 and MgO. No evidence for the high pressure form of spinel [Liu, 1978] was observed. No definite evidence of spinel was detected from shots 884 and 919. This is perhaps surprising for the latter shot, however a

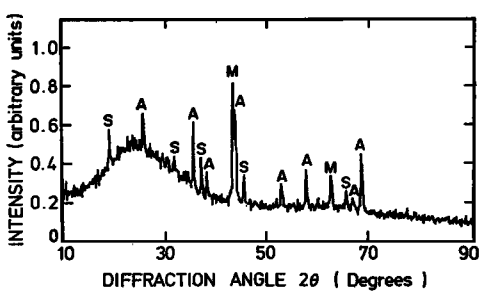

Fig. 3. Debye-Scherrer X-ray diffraction pattern of material recovered at Al_2O_3/MgO interface of shot # 905. A, M and S represent Al_2O_3, MgO and $MgAl_2O_4$ spinel peaks respectively. The spinel peaks shown gave d spacings of 4.667 Å, 2.850 Å, 2.432 Å, 2.015 Å and 1.425 Å. The data analysis program also picked out a 'spinel' peak at $2\theta \approx 77.1^\circ$ (d = 1.235 Å), however this is not labelled due to uncertainty in its significance above the noise level.

significant volume of material was missing from the recovered sample. It is possible that this occurred due to localised vaporisation. Weast [1982] gives vaporisation temperatures for Al_2O_3 and MgO as 2980 K and 3600 K.

Discussion and Conclusions

Grain sliding of single crystals of Al_2O_3 and MgO in contact was induced by oblique shock impact. Under certain conditions a spinel layer of composition $MgAl_2O_4$ and thickness ≤ 20 μm was formed at the interface between the two crystals. Although the calculated shock continuum temperatures were insufficient to melt the initial oxides, we propose that grain sliding friction at the interface induced some localised melting. Some evidence for this came from SEM observations of melt voids and dendritic stringers (Figure 4(a)). We have also observed melt layers (~ 40 μm - 300 μm thick) at copper/stainless steel interfaces in similar oblique shock experiments. In the Al_2O_3/MgO cases the melting points are higher than those of the above metals, however the thermal conductivities are much lower. Hence any heat generated at the interface would not be conducted away as quickly, and so it is quite feasible that temperatures at the interface could reach the melting points. Further evidence for similar frictional melting came from SEM observations of shear bands in the Al_2O_3 single crystals of the present oblique shots and a series of planar shots (see Figures 4(b) and (c)). Note that each shear band could be regarded as a smaller version of the crystal - crystal sliding arrangement shown in Figure 1. The high temperatures likely to have been generated at the crystal - crystal interface in all the above cases are consistent with previous experiments where the observed heterogeneous shock-induced temperatures were higher than the calculated continuum values [Kondo and Ahrens, 1983; Schmitt and Ahrens, 1983; Schmitt et al., 1986].

We have considered an alternative interpretation of our results in terms of a solid state reaction. Although directly

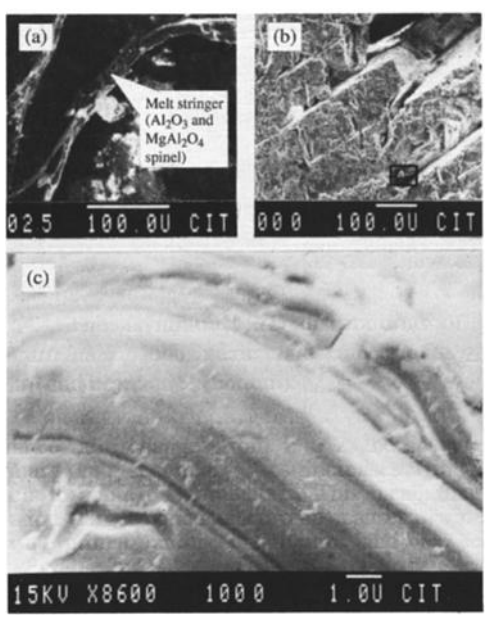

Fig. 4. SEM images of melt features and shear bands. (a) Curved dendritic stringer (mainly Al_2O_3) at interface near section IJ (shot # 905). Scale bar = 100 μm. (b) Shear bands in Al_2O_3 (planar shot # 891). Scale bar = 100 μm. (c) One limb of arched melted bleb at a shear band (outlined in (b)). Note melt void (bottom left) and curved groove indicating ductile/plastic behaviour. Scale bar = 1 μm.

relevant data appear to be scarce, Schmalzried [1981] reviews results for a closely analogous solid state reaction of NiO and Al_2O_3 to produce $NiAl_2O_4$ spinel. At 1300°C (i.e. even higher than our calculated continuum temperatures) the reaction follows a parabolic rate law of the form $\Delta x^2 = 2\bar{k}t$, where Δx is the reaction layer thickness and $\bar{k}$ is the practical reaction rate constant ($2\bar{k} \approx 1 \times 10^{-11}$ cm^2/s in this case) related to the diffusion coefficient of the rate determining ions. In our experiments the shock pulse duration $t \sim 1$ μs would give $\Delta x \approx 3 \times 10^{-5}$ μm for the $NiAl_2O_4$ layer during the shock state. Assuming that Δx for the $MgAl_2O_4$ spinel case is not grossly different than the case of $NiAl_2O_4$ spinel, then Δx for solid state diffusion (during the shock state) is much less than the observed reaction zone thickness of up to 20 μm. However, the possibility that defect enhanced solid state diffusion, subsequent to loading and unloading, might account for the observed spinel layer thickness cannot be completely ruled out. Our work might serve to highlight the need to re-examine the possible mechanisms responsible for other shock induced chemical reactions. Although Venturini et al [1985] and Morosin et al [1986] interpreted the shock produced $Zn_{1-x}Fe_xFe_2O_4$ spinel (from ZnO and Fe_2O_3 powder mixtures) in terms of a solid state reaction, a formation mechanism involving melting at grain boundaries would seem equally plausible. Melting was clearly evident in the work of Kondo et al [1986, Figure 9a] who shock produced cubic aluminium oxynitride spinel from initial AlN and Al_2O_3 fine powder mixtures.

Whether the spinel found in sediments associated with major impact events on the Earth [Kyte and Smit, 1986; Margolis et al., 1991], or that inferred from recent reflectance spectra data for certain asteroids [Burbine et al., 1992], is shock produced may be more controversial. Nevertheless, our experiments would imply that further consideration could be warranted for the shock production of spinel in these cases.

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T.J. Ahrens, Seismological Laboratory, California Institute of Technology, Pasadena, CA 91125, U.S.A.

D.K. Potter, Department of Physics, The University, Newcastle upon Tyne, NE1 7RU, England.

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